

# New fluorinated functional materials

Mario Pagliaro and Rosaria Ciriminna

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Whether in catalysis, biology or the protection of the environment, fluorinated functional materials are emerging as important chemical tools to achieve improved performance and higher stability under a variety of conditions. Providing a distinct increase in molecular hydrophobicity, fluorination allows easy tuning of a material's hydrophilic–lipophilic balance (HLB), in particular with sol–gel materials obtained by polycondensation of fluorinated precursors. Reporting on recent remarkable achievements, this review attempts to show the large unexplored potential of these materials.

## 1. Introduction

New functional fluorinated materials are rapidly emerging to meet the demanding requirements of advanced applications in fields as diverse as sensing, catalysis and environmental protection.<sup>1</sup> Indeed, in the last five years modern materials science, quantum chemistry and biochemistry have opened the way to the synthesis of new fluorinated materials possessing extraordinary properties such as crosslinkable dendrimers for the fabrication of optical waveguides of low optical loss and excellent thermal stability;<sup>2</sup> highly effective and recyclable absorbents for oil and heavy metals;<sup>3</sup> gelling polymers with excellent optical and electrical properties;<sup>4</sup> highly sensitive oxygen optical sensors;<sup>5</sup> materials for *in vivo* oxygen transport (potential blood substitutes), diagnosis and drug delivery;<sup>6</sup> liquid-crystals for high-performance displays;<sup>7</sup> self-assembling polymeric supramolecules;<sup>8</sup> high-performance catalysts for aerobic conversions in CO<sub>2</sub>;<sup>9</sup> single-wall carbon nanotubes;<sup>10</sup> photoresists for the next generation of chips;<sup>11</sup> and

thermoplastic polymers showing elastomeric behavior between –75 °C and 100 °C.<sup>12</sup>

Not surprisingly, a vast number of novel findings in functional fluorinated materials (Table 1) are being reported by the leading international scientific journals, while so called “fluorous phase” synthetic methods have evolved into mainstream chemistry practices with major suppliers of laboratory chemicals now offering fluorinated reactants and materials.<sup>13</sup>

Books and review articles on fluorine chemistry and its applications are being published on a regular basis.<sup>14</sup> Therefore, the main objective of this work is to report the emerging new applications and to outline the general

**Table 1** Number of hits provided by scientific databases for a Boolean search of “fluorinated” AND “materials” in scientific journals, books and conferences

Search engine	Hits
CASPlus:	5064
Scirus:	7262
Google Scholar:	6780

Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via Ugo La Malfa 153, 90146 Palermo, Italy. E-mail: mario.pagliaro@ismn.cnr.it



Mario Pagliaro

A research chemist at Italy's CNR based in Palermo, Mario Pagliaro carries out collaborative research with researchers in nine countries mainly in the field of sol–gel materials, catalysis, conversion of renewables, photo- and electrochemistry. A former PhD student with Arjan de Nooy and David Aynir, he has worked in the Netherlands, Israel and France. In 2005 he was appointed “Maitre de conférences associé” at the Ecole nationale supérieure de chimie in Montpellier, France.



Rosaria Ciriminna

Rosaria Ciriminna is a research chemist at Italy's CNR, working in Palermo. She started her scientific career in 1990 with a CNR fellowship to study the chemistry of Mediterranean natural products (terpenes) and has since worked at the Universities of Reading and Padova, and at Montpellier's ENCSM. Her current research interests include sol–gel hybrid materials and their application to environmentally benign processes and chemical sensing. In September 2001 she was asked to present the results of her work at the 4th World Congress on Oxidation Catalysis in Berlin.

concepts, and available methodologies, through which chemists and materials scientists using an ingenious integrated approach will be able to tailor the properties of new functional fluorinated materials for targeting specific applications. This review ends with some brief considerations of the environmental and economic aspects of fluorinated materials

## 2. Principles and methodologies

Fluorine atoms bind tightly to carbon in organic molecules and modest fluorination of the molecular structure leads to large changes in the physical and chemical properties of that molecule, imparting to fluoro-organic compounds with a variety of new functional properties, including: (i) enhanced hydrophobicity (but, high lipophobicity in perfluorinated substances), (ii) high thermal and oxidative stability (resistance to sunlight), (iii) weak intermolecular interactions, and (iv) low surface energy and surface tension. Moreover, fluorinated substances generally show: (v) a low refractive index (low light absorption), (vi) exceptional chemical and biological inertness, (vii) high gas-dissolving capacity, and (viii) high fluidity and density (for liquids).

Several fluorinating agents exist and new nucleophilic and electrophilic fluorination reactants are regularly being discovered.<sup>15</sup> Here we will briefly mention pure anhydrous tetrabutylammonium fluoride (TBAF), whose novel synthesis provides chemists with a “naked” fluoride ion acting as a nucleophile with a reactivity that is comparable to, or exceeds, that of other nucleophilic fluorinating reagents<sup>16</sup> and “select-fluor” [1-chloromethyl-4-fluoro-1, 4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate)], a highly reactive, non-toxic and easy to handle electrophilic fluorinating reagent that is replacing dangerous and less selective F<sub>2</sub> in the industrial synthesis of a variety of pharmaceutical and agricultural products.<sup>15a</sup>

Due to the anomalous physico-chemical properties of fluorinated organics, it is no surprise that fluorine incorporation into biologically active compounds, altering drug metabolism and enzyme substrate recognition, has a number of relevant consequences in life sciences.<sup>17</sup> Moreover, biochemical research recently resulted in the discovery of the first fluorinase enzyme that has the capacity to catalyze the formation of a carbon–fluorine bond:<sup>18</sup> a fundamental discovery offering a new opportunity for the preparation of organofluorine compounds as, once the gene coding for the fluorinase has been identified it will be copied and inserted into other organisms to generate novel fluorine-containing compounds by fermentation.<sup>19</sup>

The most abundant halogen element, fluorine is the most electronegative element and one of the least polarizable atoms in the periodic table. After hydrogen and helium, the fluorine atom has the smallest atomic radius (0.64 Å). The C–F chemical bond is the strongest known single bond in organic chemistry (*ca.* 450 kJ mol<sup>-1</sup>) and hydrogen atoms in hydrocarbons can be replaced with fluorine atoms to practically any extent from mono- to perfluoro-substitutions. Fluoropolymers,<sup>1</sup> in addition to the known advantages offered by other elastomers (thermoelastic behaviour, easy fibre and

coating production, traction resistance *etc.*), show pronounced hydrophobicity and high physical and chemical stability that make them suitable materials for a number of uses requiring these properties. For example, the corrosion resistance of gaseous UF<sub>6</sub> was employed in the Manhattan Project to extract the uranium isotope needed for nuclear fission; PTFE found immediate application despite its high cost and later became widely employed for coating bakeware and, in the textile industry, to make transpiring fabric from expanded porous PTFE membranes.<sup>20</sup>

### 2.1 Electronic properties and computational methods

As mentioned above, the strength of the C–F bond is unprecedented in organic compounds. Computational methods used to calculate bond energies indicate that the C–F bond energy is indeed about 450 kcal mol<sup>-1</sup> and the bond is highly polar. Fluorine in fact is much more electronegative than carbon (in the Pauling scale, C = 2.5 and F = 4.0)<sup>21</sup> which partly accounts for the extremely low refractive indices of fluorocarbons. C–F bonds also reduce the overall molecular polarizability of organic molecules by increasing the hardness of the carbon framework. What is also surprising, and explains the high stability of fluoropolymers, is the central C–C bond strength in fluorocarbons which may easily attain extremely high values (for a C–C bond) such as 112 kcal mol<sup>-1</sup>.<sup>22</sup>

Fluorinated compounds owe their unique behaviour to their peculiar electronic properties.<sup>23</sup> The C–F bond participates in strong polar interactions and the biochemical properties of organic fluorine must take into account also these polar interactions; so, the useful concept of “polar hydrophobicity” has been introduced to help in addressing some of the puzzling biochemical data of fluorinated substances.<sup>24</sup>

Finally, extensive fluorination of organic molecules generates a phase of liquid matter known as the “fluorous phase” which is the basis of the unusual behavior of heavily fluorinated molecules and polymers.<sup>25</sup> This phase does not mix with either polar or non-polar hydrogenated phases and computational research is on course to identify the minimum number of fluorine atoms that are necessary to generate a fluorous phase.<sup>26</sup>

Quantum mechanics and ever growing computational power allow the prediction of the electronic properties of an increasing number of molecules and materials; for example, prediction of the absorption spectra of fluorinated monomers leads to the preparation of molecules which impart the desired properties to the fluorinated material. Hence, for instance, theoretical absorption spectra at 157 nm for a variety of fluorinated norbornene monomers were calculated by time-dependent density functional theory.<sup>11</sup> Based on the theoretical spectra, a number of fluorinated norbornene monomers were readily prepared *via* different synthetic routes.

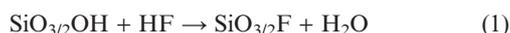
Similarly, fluorinated silica (in which elimination of surface hydroxyl groups is achieved by treatment with hydrofluoric acid solution or gas, eqn (1)) was investigated as a potential interlayer dielectric and for silica optical fibre fabrication with *ab initio* modelling and various

**Table 2** A list of low-*k* candidate materials for novel dielectrics in microelectronics

Material	<i>k</i> <sup>a</sup>
Fluorinated silica	3.2–3.6
Polyimides	3–3.5
Hydrogen silsequioxane	2.8–3.0
Methylated silica from MTMS	2.7
Fluorinated polyimides	2.5–3.0
PTFE (teflon)	1.9
Fluorinated carbon	2.1–2.5

<sup>a</sup> Measured in the out-of-plane direction at  $\nu = 1$  MHz

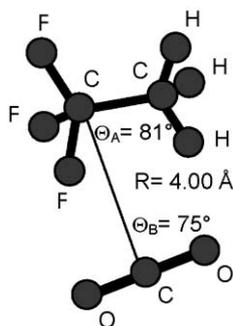
characterization techniques endeavouring to explain the dielectric constant reduction.<sup>27</sup>



The electrical and thermomechanical properties of  $\text{SiO}_2$ , in fact, are ideally suited as interlayer dielectrics in microelectronics but materials with lower dielectric constants *k* are needed for advanced interconnect applications. Fluorinated silica glass, having a dielectric constant lower than that of F-free  $\text{SiO}_2$ , is among the best low-*k* candidate materials (Table 2).<sup>28</sup>

Calculations suggest that it is the ionic component of the dielectric constant that is mostly affected by the F incorporation. Furthermore, molecular orbital calculations conducted for various cluster models of silica and for those of fluorinated silica indicate that the heat of formation of FSG *per* Si tetrahedral unit decreases with an increasing number of Si tetrahedral units (which, in its turn, depends on the preparation conditions). Remarkably, the addition of HF to silica clusters gave a F–Si bond in trigonal bipyramid geometry for a five-coordinated Si.<sup>29</sup>

As a further example, the molecular basis of  $\text{CO}_2$  interaction with fluorinated polymers has been investigated by computational chemistry on model compounds and molecular simulation of polymers such as poly(trifluoropropyl methyl siloxane) and poly[bis(2,2,2-trifluoroethoxy)phosphazene] that exhibit high  $\text{CO}_2$  permeability and preferential permeation.<sup>30</sup>



**Fig. 1** Fluorinated polymers exhibit high  $\text{CO}_2$  solubility. Calculations indicate a favorable interaction between  $\text{CO}_2$  and the polar fluorocarbon moieties and suggest that quadrupole–dipole interaction (the interaction of  $\text{CO}_2$  with the trifluoroethane moiety is shown here) is an important contribution to the total energy of interaction.<sup>30</sup>

The results indicate that  $\text{CO}_2$  forms a favorable quadrupole–dipole interaction (Fig. 1) with the fluoroalkyl groups whose maximum interaction energy ( $-11.5 \text{ kJ mol}^{-1}$ ) for  $\text{CO}_2\text{--CF}_3\text{CH}_2\text{CH}_3$  is less than typical interaction energies for hydrogen bonding, but greater than the London dispersion values for the interaction of  $\text{CO}_2$  with a carbonyl group.

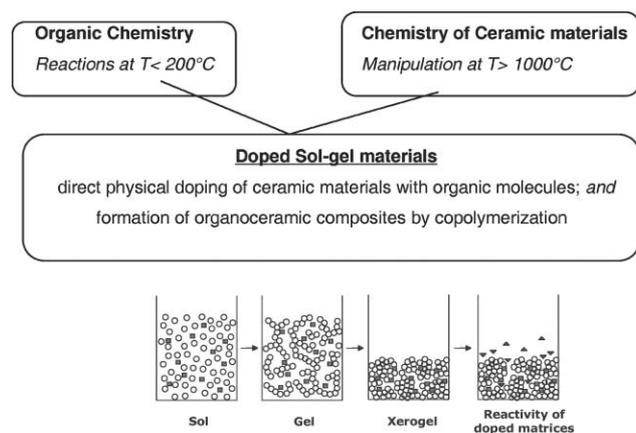
Electrostatic potential distributions indicate a small redistribution of electron density to the fluorine atoms of the trifluoroalkanes and to the oxygen atoms of  $\text{CO}_2$  in the  $\text{CO}_2\text{--CF}_3\text{CH}_3$  and  $\text{CO}_2\text{--CF}_3\text{CH}_2\text{CH}_3$  dimers. In addition, pair-correlation analysis by molecular dynamics simulation shows a strong correlation of  $\text{CO}_2$  with the trifluoromethyl group of PTFEP in agreement with the *ab initio* molecular orbital calculations which show an association of  $\text{CO}_2$  with both  $\text{CH}_3\text{CF}_3$  and  $\text{CH}_3\text{CH}_2\text{CF}_3$ . Again, these computational results not only give an explanation of the solubility of many fluorinated polymers in dense phase carbon dioxide, but suggest, for instance, that since close physical association (less than  $4.3 \text{ \AA}$  between the centres of mass) between  $\text{CO}_2$  and fluorinated groups is necessary to ensure optimal solubility, fluoropolymers with bulky groups, such as 6-F polyimides (polyimides derived from 4,4'-hexafluoroisopropylidene-diphthalic anhydride), will be considerably less soluble in this environmentally benign solvent.

Studying the effects of fluorination by crystallography and computational methods in a series of alkyl 4-[2-(perfluoro-octyl)ethoxy]benzoates, it was recently shown that fluorination determines the molecular shape of the crystal structures by making the chain rigid, whereas how the systematic change of crystal structures occurs depends on the length of the alkyl chain.<sup>31</sup> Semiempirical MO calculations showed slightly repulsive interactions between the  $\text{R}_f$  chains, and attractive ones between  $\text{R}_f$  and  $\text{R}_h$  chains and between  $\text{R}_h$  and the core of a molecular pair; thus confirming that the interactions between  $\text{R}_f$  chains are small compared with those between other moieties and that they are forced to aggregate owing to the exclusion from other moieties (see below for the experimental findings with fluorinated ORMOSILs).

## 2.2 Hybrid organic–inorganic polymers

In materials science, sol–gel science and technology have made it possible to merge the (huge) domains of organic and ceramic chemistry, allowing the preparation of highly reactive porous oxides, including fluorinated materials, doped with practically any organic molecule and, at the same time, precise control of an immense range of structural properties of the resulting materials.<sup>32</sup>

Organic compounds rarely survive temperatures above  $200 \text{ }^\circ\text{C}$ , while inorganic polymers (ceramics) are usually formed at temperatures  $>1000 \text{ }^\circ\text{C}$ . The mild, liquid-phase polycondensation of metal alkoxides typical of the sol-gel process has therefore opened the route to a vast class of extremely reactive glassy materials (doped oxides called xerogels or aerogels, depending on the drying method used to desiccate the intermediate alcogel, Scheme 1). Sol–gels have found applications in fields as diverse as optics, sensing, catalysis, electrochemistry and photochemistry due to their



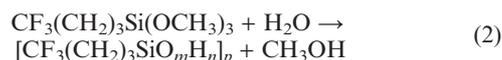
**Scheme 1** The sol-gel process to prepare highly reactive doped metal oxides unifies the domains of ceramic and organic chemistry. A sol of inorganic oxide particles is prepared by polymerization of metal alkoxides in the presence of any desired dopant molecules. The sol turns into a gel, which then dries and shrinks, forming a porous xerogel (or an aerogel, when drying is conducted with supercritical CO<sub>2</sub>) entrapping the dopant organic molecules. The pores are easily accessible by external reactants, resulting in the vast chemistry of sol-gel doped materials. Using organically modified metal alkoxides, hybrid materials are obtained amongst which fluorinated ORMOSILs are currently finding important applications.<sup>33</sup>

high sensitivity to external reactants, transparency and enhanced chemical and physical stability.<sup>33</sup>

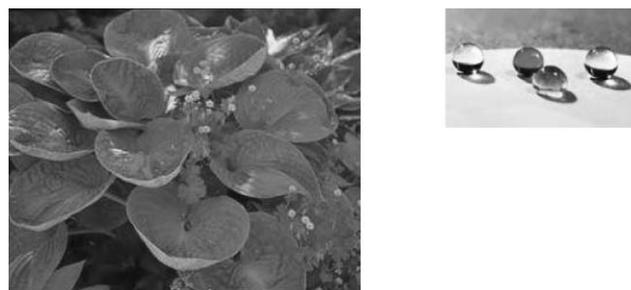
In the case of fluorinated substances, fluorine being easily bound to carbon in hydrolytically-stable metal alkoxides, a wide variety of fluorinated alkoxide precursors are easily synthesised which can be used for the synthesis of hybrids with several potential applications.<sup>34</sup>

Fluorinated ORMOSIL (organically modified silicates), in particular, are finding a number of remarkable applications due to the extraordinary properties imparted by fluorine to these organic-inorganic nanocomposites. In general, in fact, fluorination of the inorganic matrix largely enhances its thermal and chemical stability as well as the surface properties of fluorocarbon hybrid gels resulting in higher hydrophobicity and oleophobicity than in hydrocarbon ORMOSIL homologue gels.<sup>35</sup>

In particular, best results in terms of thermal stability and hydrophobicity are observed for materials produced by sol-gel hydrolysis of fluoroalkyl mono-functional trimethoxysilanes such as that represented in eqn (2) with the fluorocarbon moieties ending segregated at the surface of the material's cages



This directly affects the reactivity and sensitivity of the final doped ORMOSIL materials because in the case of doped sol-gels, the reaction takes place at the cage's surface where the entrapped dopant molecules are accessible to external reactants. Finally, the optical properties of highly fluorinated and photosensitive ORMOSIL-derived films make them



**Fig. 2** The hydrophobic behaviour of a lotus leaf (left) can be mimicked by fluorinated polyelectrolyte surfaces (right, photo courtesy of Prof. J. B. Schlenoff) in which water droplets form spheres on a silicon wafer coated with a fluorinated polyelectrolyte multilayer film roughened with clay nanorods.<sup>37</sup>

suitable for use as optical waveguides due to their low refractive index and energy absorption along with excellent UV-imprinting properties.<sup>36</sup>

### 3. Applications

In the following, a selection of novel applications of fluorinated materials is reviewed in order to show the impressive versatility of these materials and how, in practice, the concepts highlighted above are being applied by chemists and materials scientists.

#### 3.1 Hydrophobic surfaces

Hydrophobic fluorinated surfaces have a number of useful applications. In nature, a hydrophobic effect is observed on the leaves of the lotus plant due to the microscopic roughness of the leaf surface decorated with hydrophobic wax; this hydrophobic behaviour can be mimicked by ultrahydrophobic fluorinated nanocomposite films (*i.e.* surfaces exhibiting large water-contact angles) (Fig. 2).

In one approach, fluorinated polyanions and polycations are used to coat the particles of the mineral attapulgite with a hydrophobic layer, forming clusters which produce micrometre scale roughness.<sup>37</sup> Hence, a sequential layer-by-layer tri-strata assembly approach is used to produce the ultrahydrophobic surfaces: the first stratum consists of several layers of pairs of poly(diallyldimethylammonium) cations [PDADMA] and poly(4-styrenesulfonate) anions deposited from a salt solution onto a silicon wafer; the second stratum consists of alternating layers of clay particles bearing a negative surface charge and PDADM and the final stratum is made of layers of two fluorinated polyelectrolytes.

Using a similar approach, the tidy topography of the lotus leaf is mimicked using a simple, water-based process, in which micrometre-sized pores are first created on a polyelectrolyte multilayer surface (by adding acid), and then silica nanoparticles are deposited onto the material, followed by a semifluorinated silane coating. The material retains its superhydrophobic character even after being immersed in water for a week, while elimination of the semifluorinated silane coating step, makes the material super-hydrophilic.<sup>38</sup>

Having a low coefficient of friction and being inert like many fluorinated surfaces, these materials are potentially useful for the development of materials with bioadhesive (or bioinert) surfaces, thus favouring (or preventing) protein adhesion depending on the surface charge and on the tuneable HLB of the polyelectrolyte multilayers. Indeed, cells cultured on the hydrophobic surface of a positive fluorinated polyelectrolyte spread and adhere, whereas cells cultured on a hydrophilic surface of multilayers of a zwitterionic copolymer do not adhere.<sup>39</sup>

Another example of the enhanced sorption properties of fluorinated materials is provided by self-cleaning coloured materials obtained by simple treatment with a fluoroalkylsilane of a mesoporous silica gel in which striking colors, like those of butterfly wings, come from light diffracting off the ordered silica nanostructure and hydrophobicity benefits the material by shedding water and dirt.<sup>40</sup>

### 3.2 Separation and environmental protection

Fluorous solid-phase extraction is used for quick separations of reaction mixtures involving fluorous reagents, protecting groups, tags, and scavengers using silica gel bonded with perfluoroalkyl chains which separates compounds based on fluorous content.<sup>41</sup>

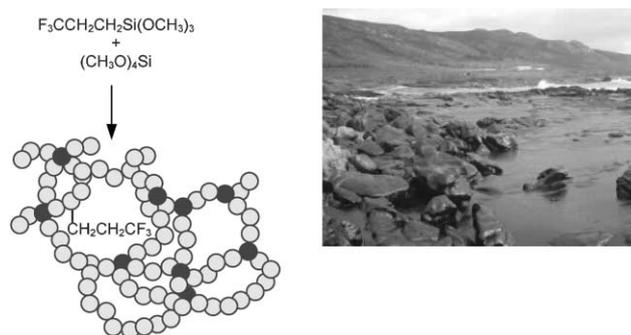
Fluorous molecules are selectively retained while non-fluorous compounds are eluted regardless of polarity. This results in a simple two-step separation of fluorous compounds from non-fluorous compounds, giving a purity comparable to traditional chromatography, but much more quickly. Hence, following completion of a reaction using a fluorinated molecule, the reaction mixture is loaded onto a fluorinated solid phase. Using a fluorophobic wash, the non-fluorous organic compounds are washed off the material while the fluorous compounds are eluted using a fluorophilic second wash.

Multiple fraction collection and analysis are not required as there is one organic wash and one fluorous wash. Due to the large separation, loading levels can be very high, and since the separation process is highly reproducible and functional group independent, it can be easily automated.

The chromatographic properties of sol-gel materials, true chemical sponges that absorb and concentrate molecules at their enormously vast (several hundreds of square metres per gram) inner surface,<sup>32</sup> can be efficiently exploited using fluorinated sol-gels as highly efficient absorbents in a wide variety of environmental decontamination applications ranging from oil-spill cleanup to removing metals and organics from aqueous and vapour media.<sup>42,3</sup>

Hence, hydrophobic aerogel ORMOSIL with extremely high surface areas prepared by sol-gel processing of 3,3,3-trifluoropropyl-trimethoxysilane and TMOS (tetramethyl-orthosilicate) can separate oil from an oil/water mix, absorbing 4–16 times their own weight of oil (Fig. 3).

Remarkably, the oil-filled aerogel remains solid and can be simply picked off the sea's surface. The excellent accessibility of the ORMOSIL matrix allows easy washing after absorption so that the targeted metals and/or organics can be removed and recovered and the composite material recycled. Since



**Fig. 3** Fluorinated ORMOSIL are capable of absorbing 4–16 times their weight of oil; a discovery of fundamental relevance to environmental protection as the impact of oil spills depends on where the oil ends up (right, the Spanish shores near Bilbao are shown after a shipwreck in 1999).<sup>42</sup>

expensive sol-gel oxides are easily coated on less expensive materials like charcoal or sintered glass beads,<sup>43</sup> fluorinated ORMOSIL are soon likely to find practical use as high-capacity and reusable absorbents for organics and metals in contaminated sites as the sol-gel process versatility allows the chemical sorption properties of the solid material to be tailored to the desired target, such as uranium, chromium, gold or VOCs (volatile organic compounds).<sup>3</sup>

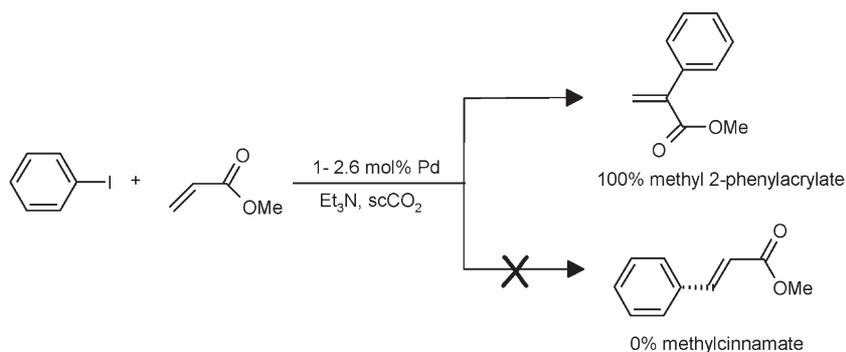
The potential benefit of this discovery is better understood when one considers that the environmental impact of an oil spill depends on where it ends up, rather than on the absolute amount of oil spilled; and that the greatest impacts occur when oil enters sensitive near-shore habitats such as coral reefs and mangroves whose recovery, once damaged, can take decades.

### 3.3 Catalysis and polymer synthesis

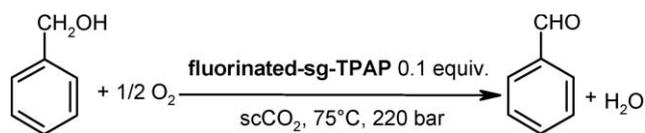
Fluorous biphasic catalysis, *i.e.* homogeneous catalytic conversions carried out within a fluorous reaction mixture in which a fluorinated catalyst, organic solvent and reagents share a single phase at the operating temperature and then separate out upon cooling to give easy catalyst separation and recovery, has now been developed as a synthetic tool.<sup>14b</sup>

Applications of fluorinated materials to heterogeneous catalysis, however, are at least as relevant as numerous. As mentioned above, fluorine and fluorine-containing compounds show a strong affinity for CO<sub>2</sub>, and heavily fluorinated polymers, being soluble in dense phase carbon dioxide (or “supercritical”, scCO<sub>2</sub>),<sup>44</sup> are ideally suited for reactions in this alternative chemical solvent which has recently found practical use in industry for the heterogeneously catalysed synthesis of several fine chemicals.<sup>45</sup>

Hence, fluorinated dendrimer-encapsulated Pd nanoparticles are active and highly selective for both the reduction of styrene and the carbon-carbon bond forming Heck reaction in scCO<sub>2</sub> (Scheme 2), with facile catalyst recovery.<sup>46</sup> The dark-brown catalyst was easily solubilized in liquid- and scCO<sub>2</sub> (dull-orange solution), with no signs of aggregation or precipitation.



**Scheme 2** Using fluorodendrimer-encapsulated Pd nanoparticles in  $\text{scCO}_2$ , iodobenzene can be coupled with methylacrylate to yield exclusively methyl 2-phenylacrylate.<sup>45</sup>

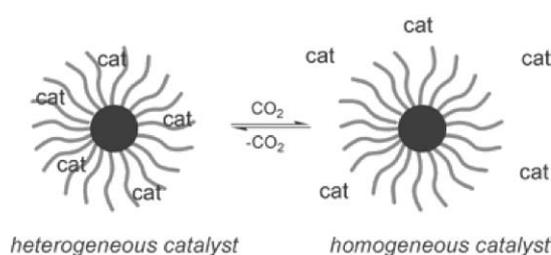


**Scheme 3** Using a fluorinated ORMOSIL-encapsulated Ru catalyst, alcohols dissolved in  $\text{scCO}_2$  are neatly converted into carbonyls with striking selectivity.<sup>9</sup>

With a similar approach, the aerobic oxidation of alcohols in  $\text{scCO}_2$  resulted in a significant improvement of the material's catalytic activity and selectivity compared to the non-fluorinated analogue in the case of either Pt and Pd supported over a fluorinated graphite;<sup>47</sup> and of perruthenate encapsulated in a fluorinated ORMOSIL (sg-TPAP in Scheme 3).<sup>9</sup> The general idea is simple: the catalyst is entrapped in a porous sol-gel fluorinated matrix; the alcohol substrate and  $\text{O}_2$  dissolve in dense phase carbon dioxide which, upon contact with the powdered hydrophobic sol-gel material, spills the reactants into the pores where the catalyst is entrapped and where the oxidative dehydrogenation takes place, and then it extracts the products.

A thorough choice of the material precursors and sol-gel polycondensation conditions is crucial in affording effective oxidation catalysts as the best activity in a series of increasingly fluorinated ORMOSIL was observed with the fluorinated silica matrix with the low degree of fluorination (10% in molar terms), pointing to a balance between the  $\text{CO}_2$ - and  $\text{O}_2$ -affinity of the matrix and the (relatively polar) alcohol substrate, thus showing how the HLB of a fluorinated sol-gel oxide can be tuned to optimise, for instance, the catalytic activity.

Fluorinated moieties in organic molecules, in fact, are known to segregate from other functional groups (see above in section 2.1), whereas in the growing sol-gel material micelles easily form with the hydrophilic heads pointing towards the strongly hydrogen bonding water/methanol solvent interface and the hydrophobic moiety entrapping the hydrophobic dopant molecules.<sup>48</sup> Therefore, reaction conditions are chosen to minimise such micellization and to prevent burying the reactive dopant molecules in the bulk of the final xerogel.



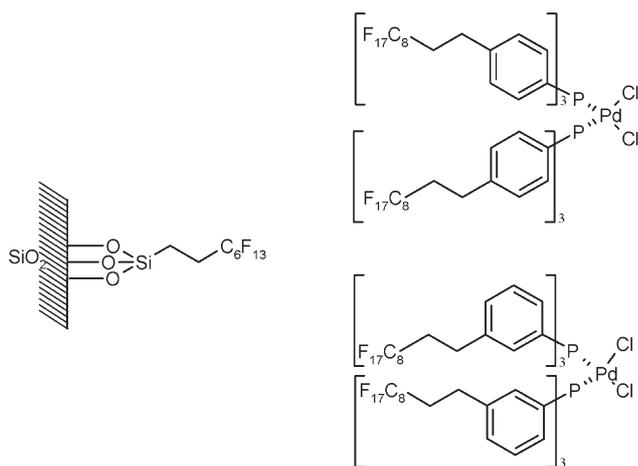
**Fig. 4** Use and recovery of a homogeneous catalyst with carbon dioxide as a solubility switch is made possible by fluorinated silica gel such as that shown below which replaces the fluorous solvent in fluorous biphasic catalysis.<sup>49</sup>

Further extending a similar approach, fluorous biphasic catalysis can be conducted in (subcritical) carbon dioxide used to expand a traditional organic solvent and boost solubility thereby replacing the fluorous liquid with fluorinated silica. In this manner, the fluorous catalyst is induced to dissolve in the organic solvent by the presence of  $\text{CO}_2$ , and the recovery of the catalyst after the reaction is achieved by simple release of the  $\text{CO}_2$  pressure (Fig. 4).<sup>49</sup>

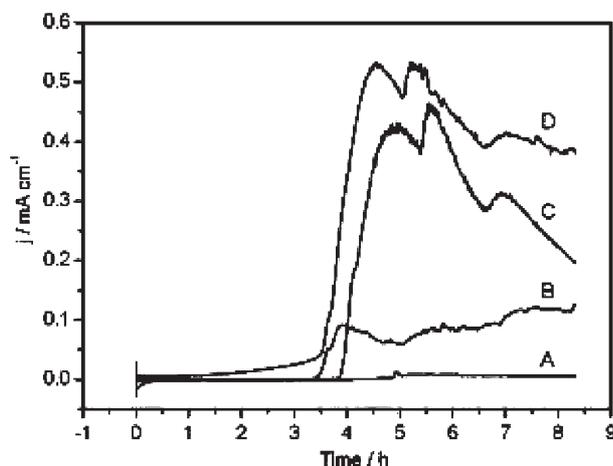
Similarly, the immobilization of a perfluoro-tagged palladium catalyst on a fluorinated silica gel affords a recyclable catalyst whose activity in the Suzuki and Sonogashira cross-coupling reactions is comparable to those found in liquid-liquid fluorous biphasic catalysis (Fig. 5).<sup>50</sup> No fluorous solvent was needed for the reaction and the isolation and recovery of the catalyst absorbed at the ORMOSIL surface, very small amounts of catalysts could be easily handled and the same support can be used for different catalysts, without the need for a separate linker unit.

Stability enhancement upon fluorination can be also exploited to achieve superior performance in heterogeneous catalysis. Hence, fluorinated polyanilines outperform the parent compound polyaniline as the electrode modifier in electrodes consisting of a platinum electrocatalyst covered by a conductive polymer like polyaniline; these are excellent anodes for harvesting electricity in microbial fuel cells.<sup>51</sup>

Similarly to polyaniline, they improve the catalytic activity of the platinum towards the oxidation of hydrogen, a product



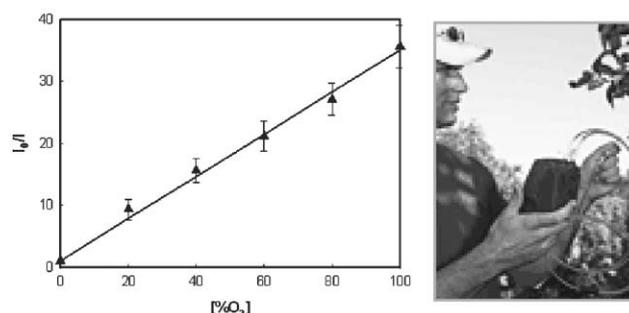
**Fig. 5** Ideal fluorous biphase catalysis uses no fluorous solvent: this fluorous Pd catalyst supported on fluorous silica selectively mediates Suzuki and Sonogashira reactions and it is easily recovered and recycled over several cycles.<sup>50</sup>



**Fig. 6** The current responses of poly(tetrafluoroaniline) and a poly(2-fluoroaniline) modified platinum electrodes are superior (curves C and D) in their catalytic activity compared to the non-fluorinated polyaniline modified electrode (curves A and B).<sup>51</sup>

of the anaerobic microbial metabolism (Fig. 6). Compared to polyaniline, however, the fluorinated polymers are superior in the protection of platinum from becoming poisoned by metabolic by-products. The high stability of poly(2,3,5,6-tetrafluoroaniline) towards microbial and chemical degradation makes this compound a highly promising candidate for applications in microbially aggressive environments like sewage sludge.

Finally, fluorinated solvents allow the synthesis in supercritical CO<sub>2</sub> of polymer chains with a very narrow molecular weight distribution as well as synthesis of block copolymers using the “controlled” free-radical polymerization techniques known as atom transfer radical polymerization (ATRP), and removing the catalyst in an elegant way.<sup>52</sup> Hence, for example, using Cu(0), CuCl, a functionalized bipyridine



**Fig. 7** A fluorinated ORMOsil doped with Ru is a highly sensitive O<sub>2</sub> sensor. The fluorine ensures unprecedented sensitivity and remarkable stability (2% drift over six months) and the material is being implemented in sol-gel hand-held oxygen sensors that have been commercialized already (right, photo courtesy of Ocean Optics Ltd).<sup>53</sup>

ligand, and an alkyl halide initiator, block copolymers comprised of fluorinated (meth)acrylates and poly(MMA) (MMA = methyl methacrylate) or poly(DMAEMA) (DMAEMA = 2-(dimethylamino)ethyl methacrylate) were recently produced in scCO<sub>2</sub> by ATRP.<sup>53</sup>

### 3.4 Sensors and analysis

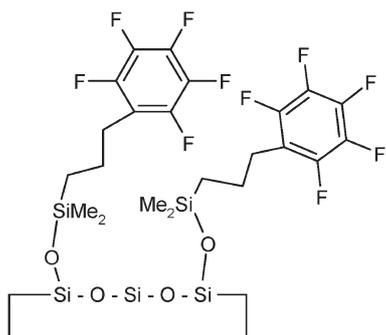
By exploiting the enhanced O<sub>2</sub> diffusivity across fluorinated substances<sup>6</sup> and their unique physical and chemical stability, it was discovered recently that the O<sub>2</sub> sensitivity of a hybrid xerogel-based quenchemetric sensor composed of *n*-propyltrimethoxysilane and 3,3,3-trifluoropropyltrimethoxysilane doped with the luminophore tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) ([Ru(dpp)<sub>3</sub>]<sup>2+</sup>) is extremely high (Fig. 7).<sup>5</sup>

Such a sensor shows a stable response (constant to within 2%) over a six month period, compared to the five-fold decrease in sensitivity in pure SiO<sub>2</sub>-based xerogels) and exhibits a sensitivity significantly greater than observed with any previous [Ru(dpp)<sub>3</sub>]<sup>2+</sup>-based quenchemetric sensor. These findings open the way to the commercial development of second-generation sol-gel oxygen optical sensors that are replacing earliest electrochemical methods to detect this ubiquitous reactant with fast, economic optical detection (Fig. 7, right).<sup>54</sup>

Another advanced application of the increased hydrophobicity of fluorinated interfaces in chemical analysis was recently reported in which detection limits about 50 times more sensitive than any previously obtained by mass spectrometry were achieved.<sup>55</sup>

The technique is based on a soft ionization method in which porous silica surfaces are used to generate gas-phase ions, which are then mass-analyzed. Simple organic modification of the porous silica surface with fluorinated silanes (Fig. 8) largely improves the sensitivity and also enables the surface to absorb analytes from solution selectively, *via* hydrophobic interactions, allowing extraction (by selective surface absorption) of tiny amounts of analytes from complex matrices containing salts and other contaminants that impede MS analysis without any purification.

Thus, in a series of dilution experiments aimed to demonstrate the sensitivity of the method measuring solution



**Fig. 8** Using a fluorinated (pentafluorophenyl-functionalized) ORMOSIL matrix in the technique called desorption-ionization on silicon (DIOS), an impressive detection limit of 480 molecules (800 yoctomole) was achieved.<sup>54</sup>

concentrations of a peptide commonly used as a sensitivity standard, an impressive lower detection limit of 480 molecules (or 800 yoctomoles:  $800 \times 10^{-24}$  mol) was reliably achieved.

#### 4. Economic and environmental aspects

In the 60 years since the serendipitous discovery of PTFE [or poly(tetrafluoroethylene)] in 1938, the chemistry of fluorinated organics has evolved into a well established and articulated research field,<sup>14</sup> and a prosperous industry,<sup>56</sup> in which partly and perfluorinated compounds are prepared either for enhancing the original functionality of the organic compounds (for example, the bioactivity) or for imparting various unique functions originating a cornucopia of applications (Fig. 9).

As might be expected with highly stable and hydrophobic compounds, however, besides the ozone layer depletion action of chlorofluorocarbons, fluorinated materials have a number of environmental and health impacts that have yet to be fully



**Fig. 9** Nobel physicist Richard Feynman drops a sample of the rubber O-ring into a glass of iced water in front of the US government commission that investigated the 1986 Space Shuttle disaster revealing the lack of resiliency of the rubber O-rings that held sections of the solid rocket boosters together when cooled to 0 °C. Today the Shuttle uses O-rings made of fluoroelastomers capable of retaining elasticity over a wider temperatures range.<sup>57</sup>

assessed,<sup>58</sup> while global production of fluorochemicals is rising rapidly.

For instance, the surfactant perfluorooctanoic acid (PFOA) used to manufacture PTFE and related waterproof fabrics persists in the environment and causes developmental and other adverse effects in laboratory animals. The compound was found in the blood of people across the world, including those living thousands of miles from the manufacturing sites.<sup>59</sup> Eventually, in June 2005, a report from the US environmental protection agency (EPA) science advisory board concluded the agency should classify the chemical as a “likely” carcinogen in humans.

Therefore, as research on the health, safety and environmental aspects of fluorinated substances is due to provide reliable data soon,<sup>60</sup> production methods should be implemented which are compatible with the environment and with the health of the workers. This means, for instance, that zero-waste production processes should be developed along with a full recycling logic, that in this case is further justified by the high cost of fluorinated organics. Alternatively, the use of fluorinated solvents in fluorous catalytic synthesis can be entirely be prevented by designing catalysts that become soluble in the organic solvent on raising the temperature of the mixture,<sup>61</sup> or, even better, that do not require fluorous solvents at all (Fig. 5).

On the other hand, it may also be noted that fluorine-based surfactants are helping, as solvent boosters, to replace toxic and carcinogenic chlorinated solvents in the dry cleaning industry with supercritical CO<sub>2</sub>: an economically and environmentally viable technology that is now spreading in the EU after its launch in the US in the mid 1990s.<sup>62</sup>

Clearly, the precautionary sustainability principle here would be to recommend more developments that, like the latter, are beneficial to the economy as well as to the environment. Since fluorine chemistry is a technologically advanced enterprise practiced by leading chemical companies, it might well reveal a field where chemical industry’s new approach to sustainability based on radical productivity increases in resource utilization and production of entirely recyclable products will be implemented at large.<sup>63</sup>

#### 5. Conclusions and future challenges

Fluorinated materials are a vast class of high-performance functional substances having a multitude of applications. Fluorine imparts distinctive properties to fluorinated materials which are increasingly understood (and predicted) in the light of modern developments in quantum chemistry. Furthermore, new materials science and biochemistry methods allow the preparation of sophisticated fluorine-containing materials for targeting advanced applications which are likely to enter ever increasing sectors of modern life. In this sense, the large potential of fluorinated materials remains largely unexplored; the judicious integration of these disciplines will make new strategic applications possible amongst which, biotechnological syntheses and catalytic conversions are only few of the possible novel developments.

In the early 1990s researchers at a petrochemical company were trying to develop a three-way oxidation catalyst to

selectively convert methane to methanol, with the idea of mimicking the behaviour of the methane monooxygenase enzyme discovered in the early 1980s.<sup>64</sup> The eventual outcome was fluororous phase catalysis as the development of such catalyst was found to be “exceedingly difficult”. The problem of converting natural gas into a valuable oxygenates, however, remains the central problem of heterogeneous catalysis in the petrochemical industry<sup>65</sup> and, therefore, for the global society which continues to burn methane for heat and electricity and so represents a major form of waste.

Similarly, membranes made of the fluorinated polymer Nafion (a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups created by introducing sulfonic acid groups into the bulk polymer matrix of Teflon) has been applied over the past 30 years in fuel cells, thanks to their durability and excellent performance. As the development of new materials for fuel cells is rapidly expanding, novel fluoropolymers will be introduced<sup>66</sup> to meet increasingly demanding requirements as in the case of maintaining stable cell operation for photovoltaic dye-sensitized nanocrystalline solar cells upon prolonged use at 80 °C (where a heat resistant quasi-solid state electrolyte mainly based on a fluorinated polymer is used).<sup>67</sup>

New fluorinated materials will play a major role in these and other relevant societal advancements and, as the number of research problems remains open, fluorine chemistry will continue to be a fascinating field of research for many years to come.

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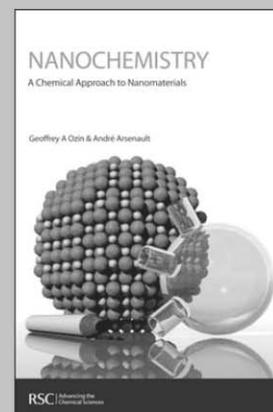
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